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PVP Protective mechanism of palladium nanoparticles obtained by sonochemical process

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Abstract

The protective effect of polyvinylpyrrolidone (PVP) on the palladium nanoparticles has been investigated using Fourier Transform Infrared Spectroscopy (FT-IR). Palladium nanoparticles have been obtained by ultrasonic irradiation of $Pd(NO_3)_2$ solution in presence of ethylene glycol (EG) and PVP. The sonochemical reduction process of palladium ions (Pd(II)) to palladium atoms (Pd(0)) can be explained by considering the intense ultrasonic waves that are strong enough to produce cavitation: formation, growth and collapse of bubbles. The UV-Visible absorption spectroscopy revealed that the reduction of Pd (II) to metallic Pd has been successfully achieved. The FT-IR spectroscopy spectra analysis show that, in presence of ethylene glycol, the stabilization of the nanoparticles results from the adsorption of the PVP chain on the palladium particle surface via the coordination of the PVP carbonyl group to the palladium atoms. The transmission electron microscopy (HRTEM) and electron-dispersive X-ray (EDX) results confirm the dispersion, the nanometric size and the composition of the obtained palladium particles.

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Keywords: Palladium nanoparticles; Protective agent; UV-Visible spectroscopy; FT-IR spectroscopy; MET; EDX.

1. Introduction

Nanoscale materials have received considerable attention because the particles with nanometric size range are thought of as a bridge between molecules and bulk materials [1]. These nanomaterials often exhibit very interesting chemical, optical, electronic and magnetic properties that are unachievable in bulk materials which open the way to the new applications which mark the beginning of the era of nanotechnology [2]. Moreover, ultrafine particles of

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noble metals have attracted particular interest because their increased number of edges, corners and faces give them a high surface/volume ratio and therefore are useful in various fields of chemistry.

Several synthetic approaches and different metal precursors have been applied to generate palladium nanoparticles having different shapes and sizes [3-5]. In order to prevent the formation of undesired agglomerates of palladium nanoparticles, the processes have been performed in the presence of various surfactant molecules. The ultrasonic reduction method of palladium salts in various media has been used to generate novel palladium nanoparticles with much smaller size, higher surface area and narrow size distribution than those prepared by other methods [6, 7].

In this work, we present the study of the palladium nanoparticle formation obtained by sonochemical reduction of palladium (II) nitrate solution and the protective role of polyvinylpyrrolidone (PVP).

2. Experimental procedure

A mixture of 0.5 mL of $Pd(NO_3)_2$ solution (Aldrich), 250 mg of PVP (Aldrich) and 40 mL of ethylene glycol (Prolabo) was irradiated in a covered and fixed vessel using a multi-wave ultrasonic generator (30 kHz).

The UV-Visible absorption spectra were obtained by an UV-Visible spectrophotometer from Hitachi. The protective action of stabilizer agent was investigated using Fourier Transform Infrared Spectroscopy (FT-IR) using an ATI Matson Genesis series FTIR. The palladium particles shape and size were investigated using transmission electron microscopy (HRTEM, Topcon 002B operating at 200 kV).

3. Results and discussion

3.1. Palladium (II) ions reduction

The sonochemical reduction of palladium (II) ions (Pd(II)) to palladium atoms (Pd(0)) can be explained by considering the intense ultrasonic waves that are strong enough to produce cavitation [8,9]. Dhas et al. [10] suggest that, because of the low vapour pressure of the palladium complex, the major sonochemical reduction of Pd(II) to Pd(0) takes place in the interfacial and the bulk regions. The collapsing cavity will enhance the dispersion of the radicals and the palladium ions which increases the probability of meeting of the active centers. In addition the presence of the shear forces of the polymer (PVP), may, also, participate at the formation of intermediate radicals (R) such as $^{\bullet}H$, $^{\bullet}CH_3$, $^{\bullet}CH_2R$, etc [11]. According to this explication and on the basis on previous studies [8, 9, 12], it is assumed that the sonochemical reduction of Pd(II) ions will occurs according to the flowing steps:

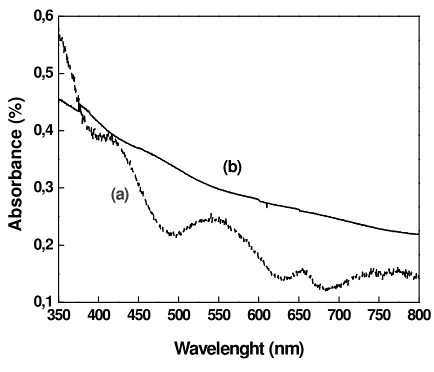

Fig 1:UV-Visible absorption spectra of (a) starting solution, (b) irradiated sample.

$$H_2O \xrightarrow{\text{Ultrasonic irradiation}} {}^{\bullet}OH + {}^{\bullet}H \qquad (1)$$
$$H + {}^{\bullet}OH\ ({}^{\bullet}H) \longrightarrow {}^{\bullet}R + H_2O\ (H_2) \qquad (2)$$
$$Pd(II) + {}^{\bullet}R \longrightarrow Pd(0) + RCHO + H^+ \qquad (3)$$

$$nPd(0) \longrightarrow Pd_n \text{ dispersed} \qquad (4)$$

Figure 1-a exhibits the UV-Visible absorption of starting solution. The spectrum presents absorption peaks at 540 and 340 nm attributed to the palladium complexes species present in the solution [12, 13]. These absorption peaks disappeared in the spectrum of irradiated sample (Figure 1-b). This result indicates the reduction of the Pd(II) ions to Pd(0) [8].

3.2. Palladium nanoparticles identification

The palladium suspension spectrum (Figure 1-b) shows a continuous absorption rise in the background towards higher energies due to Mie scattering from the palladium nanoparticles in the solution [14].

The chemical analysis of palladium nanoparticles can be confirmed by Electron-dispersive X-ray spectral analysis. The EDX spectrum (Figure 2) of irradiated sample proves clearly the presence of single palladium particles. The Cu peaks originate of scattering from the cooper mesh support grid.

TEM micrograph of the irradiated colloid is presented in figure 3. The micrograph analyses shows that, the sonochemical reduction of Pd(II) leads to the formation of monodispersed palladium particles having a rounded shape and a diameter of about 5 nm.

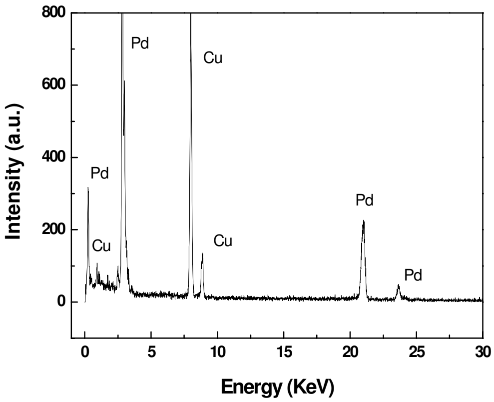

Fig 2: Electron-dispersive X-ray spectrum of irradiated sample

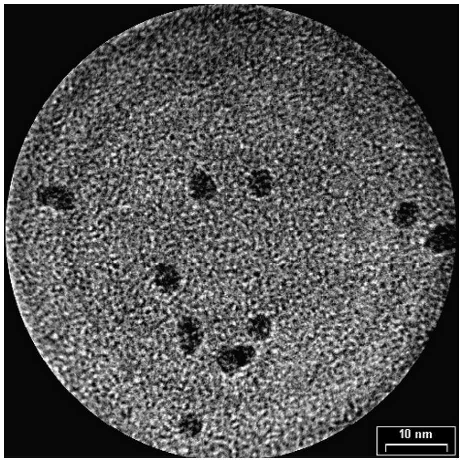

Fig 3: TEM micrograph of irradiated sample.

3.3. Palladium nanoparticles stabilization

The stabilization of nanoparticles has been investigated using the FT-IR spectroscopy. The obtained spectrum of palladium nanoparticle solution is shown in figure 4. The absorption band appearing at 1645 cm^{-1} is assigned to the stretching vibration mode of the poly(vinylpyrrolidone) carbonyl, C=O (PVP), in the nanoparticle suspensions. Széraz et al. [13] have studied the solvent effect on the adsorption of PVP molecules on γ-Alumina. The shift of the carbonyl group position towards low frequencies has been assigned first to the interaction between the EG and the

PVP and second, to the adsorption of PVP molecules on the γ-Alumina surface. Moreover, during the preparation of PVP/Sodium Montmorillonite nanocomposite, Koo et al. [14] attributed the shift of the C=O (PVP) absorption towards low frequencies to the interaction between C=O (PVP) and the silicate surface.

In our case, the shift of the PVP carbonyl position in the EG-PVP-Pd colloid, compared to the C=O (PVP) adsorption position at 1679 cm^{-1} and to the C=O (PVP-EG) position at 1669 cm^{-1}, is essentially due to the interaction between C=O (PVP) and palladium nanoparticle surface.

This result is in good agreement with those reported in earlier studies [15-17] where it has been concluded that the PVP can protect the metal nanoparticles via the carbonyl group.

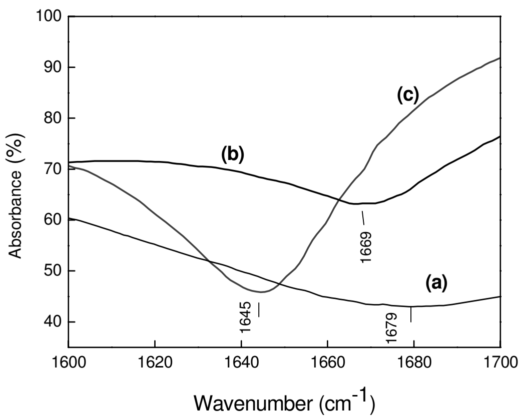

Fig 4: Spectral regions of the C=O (PVP) band intensity in FTIR spectra of (a) Pure PVP, (b) Mixture PVP-EG and (c) Irradiated sample (EG-PVP-Pd)

Conclusion

In this study, palladium nanoparticles, having a round shape and average diameter of about 5 nm, have been obtained by ultrasound irradiation of $Pd(NO_3)_2$ solution in presence of EG and PVP. The experimental results analysis shows that all Pd(II) ions are reduced to Pd(0) atoms. The PVP protects the palladium nanoparticles by the adsorption of its molecules on the particle surface via the coordination of the C=O group with the palladium atoms.

Acknowledgements

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